

REMARKS

Applicants respectfully request reconsideration of the present application in view of the foregoing amendments and in view of the reasons that follow. The amendment to claim 1 is supported by page 7, lines 15-20 and Examples 1-3 on page 9 of the specification.

Rejections Under 35 USC 102(b)

Applicants traverse the rejections under 35USC 102(b) for the following reasons.

Hayden (US 5,387,751)

The catalyst used in Hayden is a silver catalyst supported on α -alunima, which was calcined before use (see at lines 7 to 11, col. 3, and lines 52 to 53, col. 6). Hayden teaches that the catalyst is dried before use. The process of Hayden is silent on the utilization of water vapor in the epoxidation process. See the Examples.

In Example 17, a process gas stream containing 30% propylene, 8% oxygen and 1150 ppm dichlororomethane was used and the reaction was performed with oxygen selectivity/conv. of 14%/12% and 35%/6% as shown in Table 6, col. 13. The amount of oxygen that was used for undesirable side reactions other than epoxidation reaction is calculated to be less than 1%. Then the amount of water that may have resulted from such oxygen per mol of propylene in the process gas stream, or in the reaction would be far less than the recited amount in the present claim.

The Examiner mentions the chlorine-containing reaction modifier such as a Cl-C10 compound. However, it is stated that the concentration of such compound should be in the range of 0.1 to 500 parts per million parts of the reaction medium by weight. The amount of the modifier is too much small to render the presently claimed amount of water anticipated.

Hayden does not teach or disclose the amount of water that was added to the reaction in the presently claimed process either explicitly or inherently.

Boeck (US 5,618,954)

The process of Boeck is directed to epoxidation of butadiene using a catalyst containing Ag supported on α -alunima (penultimate paragraph col. 7). Boeck is silent on propylene and therefore cannot anticipate the present claims.

Nakashiro (US 6,498,122)

The process of Nakashiro is directed to the epoxidation of ethylene. Nakashiro is silent on propylene. Superheated steam is applied to the impregnated carrier to make the distribution of silver and alkali metal supported in the resulting catalyst uniform as described at lines 46 to 49, col. 4. But the production of ethylene oxide is not conducted in the presence of such superheated steam.

In connection with Boeck and Nakashiro, the applicants attach hereto as Appendix I Applied Catalysis A: General 221 (2001) 73-91 by Monnier. Monnier discloses under 3.2. Epoxidation of 1,3-butadiene, from the last paragraph on page 82 to line 5, on the right column, p.83, in Table 2 that Ag catalyst in which Ag is supported on α -alumina shows catalytic activity for oxidation of butadiene and ethylene having vinyl hydrogens only but is not suitable to epoxidize propylene and butene having allyl hydrogen atoms. In the disclosed reactions, ethylene and butadiene were converted to corresponding epoxy compounds. Propylene and butene, however, were not effectively converted to corresponding epoxy compounds.

Monnier teaches that the Ag catalyst in which Ag is supported on α -alumina, which were also disclosed as preferable or typical catalyst in Hayden, Boeck, and Nakashiro, did not show similar effect to propylene though the differences between propylene and ethylene or butadiene is just one carbon atom and the nature of hydrogens. It can be said from the teachings of these references that in the real epoxidation reactions propylene behaves rather in a different manner than ethylene or butadiene.

Therefore, the teachings of Boeck or Nakashiro cannot anticipate the presently claimed invention.

Mul (US 6,392,066)

Mul discloses the epoxidation catalyst and epoxydation reaction of ethylene, and that in the penultimate paragraph col. 7 that the feedstream may contain inert gas such as nitrogen or helium as a ballast or diluent, and mentions that carbon dioxide is not desirable in view of selectivity and should preferably be removed from the feedstream.

Water vapor is referred to in the same context in which carbon dioxide is not considered a desirable component and is to be removed.

Although during the catalyst preparation a water solution is employed it is described at the last two lines of Example 1, col. 8, that the prepared catalyst is calcined at 375°C before use.

In addition there is no mention of the addition or the effect of water vapor in the oxidation reaction as it can be seen from the descriptions (e.g. Example 5, col. 9).

The process of Mul is silent on the use of water in the epoxidation process per se and therefore, cannot anticipate the present invention.

Conclusion

Applicants believe that the present application is now in condition for allowance. Favorable reconsideration of the application as amended is respectfully requested. The Examiner is invited to contact the undersigned by telephone if it is felt that a telephone interview would advance the prosecution of the present application.

The Commissioner is hereby authorized to charge any additional fees which may be required regarding this application under 37 C.F.R. §§ 1.16-1.17, or credit any overpayment, to Deposit Account No. 19-0741. Should no proper payment be enclosed herewith, as by a check or credit card payment form being in the wrong amount, unsigned, post-dated, otherwise improper or informal or even entirely missing, the Commissioner is authorized to charge the unpaid amount to Deposit Account No. 19-0741. If any extensions of time are needed for timely acceptance of papers submitted herewith, Applicant hereby petitions for such extension under 37 C.F.R. §1.136 and authorizes payment of any such extensions fees to Deposit Account No. 19-0741.

Respectfully submitted,

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The epoxidation of olefins is an extremely important class of catalytic reaction in the chemical industry. The silver-catalyzed gas phase epoxidation of ethylene using molecular oxygen is one of the most successful examples of heterogeneous catalysts [1]. In 1938, the domestic production of ethylene oxide alone was 8.4 billion lbs [1]. In spite of the feasibility and importance of olefin epoxides in the chemical processing industry, until very recently, no olefins had been commercially epoxidized using

the allylic C-positions. While the vinyl
ether C_1 is substituted with a phenyl group, the allylic C-positions are substituted with a vinyl group.

in $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ (4-5). Thus, electrophilic attack by oxygen and abstraction of one of the allylic $\text{C}-\text{H}$ bonds in propylene becomes energetically more favorable than electrophilic addition of oxygen across the $\text{C}=\text{C}$ double bond. Once abstraction of hydrogen occurs, epoxide formation is precluded. However, lighter olefins are successively epoxidized.

obtained using indirect oxidation routes, such as the well-known peroxidation process for propylene epoxidation, whereby organic hydroperoxides or organic peroxides are reacted with propylene to produce a stoichiometric amount of propylene oxide and organic acid, respectively. For instance, the hydroperoxidation process of propylene by *tert*-butyl hydroperoxide or ethylbenzene hydroperoxide is typically conducted in the liquid phase in

In the presence of high-valent, homogeneous Mo, V, or Ti catalysts at 90–140 °C and 15–65 bar pressure to produce propylene oxide along with tert-butyl alcohol or ethylbenzene [6]. The tert-butyl hypoterpoxide or tert-butylbenzene hypoterpoxide are formed, or in a separate step from isobutane and ethylene oxide. This technology, which is well established and involves much of the commercially-produced propylene oxide, suffers from the fact that the coproducts formed during reaction are actually produced in a larger weight fraction than propylene oxide. Thus, successful application of this technology requires separation of the by-product stream. Similarly, use of

The discovery of the titanium silicic acid TS-1 by Ferri and Amato et al. [7] opened a new pathway for the preparation of oligomer clays by permitting the use of hydrogen peroxide (H_2O_2) as the indirect oxidant of the epoxidized aliphatic olefins and to form only H_2O as an environmental-friendly by-product [8]. This procedure is very selective to epoxidates, such as propylene oxide with selectivities > 95%, based on propylene oxide and 70–95% based on H_2O_2 . However, because of the relatively high cost of H_2O_2 , this process has not been commercialized to date on a large scale. Consequently, most current research and development has focused on either the use of molecular or on O_2 as the direct oxidant for selective epoxidation or on *in situ* generation of indirect oxidants, such as H_2O_2 .

2. Preparation by *in situ* generation of
oxidant using O_2 .

2.1. Preparation using transition metal complexes

Most of the earlier efforts using molecular oxygen as the *in situ* oxidant for higher olefin epoxidation have been conducted in the liquid phase using soluble transition complexes as homogeneous catalysts. Selected examples of these homogeneous and heterogeneous catalysts are summarized in Table 1. Examples that require the use of transition-metal reagents, such as *in situ* included since these undergo epoxidation are not included since these

2. Epoxidation by in situ generation of oxidant using O_2

2.1. Oxidation using transition metal complexes

Most of the earlier efforts using molecular oxygen as the *in situ* oxidant for higher olefin epoxidation have been conducted in the liquid phase using soluble metal complexes as homogeneous catalysts. Selected examples of these catalysts and performances are summarized in Table 1. Examples that require the use of hetero-atom-oxidants, such as *ab initio* included since these are used in the epoxidation.

strategies are the same as copolymerization using peroxides. In these examples cited in Table 1, most of the in-chain radicalic schemes involve reparation by free radical processes involving peroxides and hydroperoxides in solution. Thus, the overall performance is the sum of both a stepwise as well as a thermal, free radical component, making it difficult to determine the efficacy of the homogeneous catalyst. For instance, Budnik and Kochi [11] reported that when Co(II) acetofenone was used as the catalyst during the copolymerization of norbornene and *tert*-butyl acrylate, the copolymerization showed induction periods characteristic of radical chain processes. In this case β -peroxyacryloyl radicals, in these cases, (the primary mechanism for olefin epoxide formation is not catalytic, but is thermal autoxidation. As is typical of most reactions proceeding by free radical mechanisms, selectivities for the different isoplates are often unacceptable (low to high) the number of different products can lead to

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expansion economically viable. For these examples employing soluble Cu(II) and Pt(II) complexes as catalysts, however, no free radical process was operative in either case. However, both Hg(II) conventions and propionate anide selectivities were unacceptably low in both instances, typical for catalytic, olefin epoxidation reactions using soluble, transition metal complexes. Similarly, the complex system employing EuCl_3 , Zn powder, and CH_3COOH as catalysts compensated results in 1-tert-butyl epoxide formation at a turn over frequency of 13.6 h⁻¹. Clearly, the data reported in Table 1 indicate the problems often cited for the use of liquid, glassy, olefin epoxidation reactions. The carbonyl reactions are slow, giving unacceptable rates of epoxide formation; further, it is difficult to suppress free radical, chain reactions from occurring in solution. While radical reactions are much faster, they are inherently non-selective, leading to poor utilization of olefin, feedstock, and expensive separation processes to isolate the desired epoxide product. A much more complete discussion of transition metal complexes as olefin epoxidation catalysts has been compiled in an excellent review by Jorgenson [16].

2.2. *Epoxi heterocure में स्पॉन्टेनेस अवधियों की क्षमता*

A very different method for propylene epoxidation has been reported by workers in Lin Corporation [17,18]. Mullen salt mixtures, with LiNO_3 , NaNO_3 , and KNO_3 being the preferred alkali metal substrate salts, were used to assist in the epoxidation of a vapor phase feed consisting of propylene, oxygen and nitrogen at temperatures ranging from 180 to 400 °C. While the specific nature of the catalytic activity of the mullen salts is not specified nor has it been confirmed, it is believed that propylene oxide is primarily formed by the thermal reaction of propylene with oxygen, and the primary role of the mullen salt is to fluctuate as a high capacity, heat removal medium, which, catastrophically maintains an isothermal temperature profile during the highly exothermic, selective and non-selective oxidation reactions. The reaction products, which are gas stripped from the mullen salt bed, are primarily composed of propylene oxide, acrolein, allyl alcohol, and acetone as well as CO and CO_2 . For example, using a mullen salt composition of $30\text{ mol}\%$ LiNO_3 , $20\text{ mol}\%$ NaNO_3 , and $50\text{ mol}\%$ KNO_3 at a reaction temperature of 225–C and 538 psig pressure,

a feedstream containing of 33% C_2H_6 , 8% O_2 , and balance N_2 (total flow = 2000 cm 3 /min (377) was partially converted to 57% propylene oxide, 7% other C_3 -oxygens, and balance CO_2CO ; conversion of C_2H_6 was 92%. It is difficult to factor the nature of the catalyst formed by the structure of the unspent salts, although the selectivity to PO does seem higher than reported for a purely thermal, even heterothermal, oxidation reaction. The reaction is run lean in molecular O_2 , which does suggest that the reaction may be largely thermal in nature, and that selectivity is controlled by restricting O_2 concentration in the feed. Another supporting reason that the mixed metal salts may not function as true catalysts is the basis of another patent published by Olin Corporation [18]. In this patent, Meyer claims that alkylates, including isobutylene, sec-butylcyclohexane, and propylbenzylcyclohexane, are substantially isolated in small amounts during operation of the azotrop bed process, may be distilled in a second reactor to effect the co-oxidation of unspent C_2H_6 with the peroxides formed by the thermal reaction of these alkylates and O_2 . Additional propylene oxide is then formed by the well-known epoxidation by peroxide, which has been mentioned above. Thus, it is now difficult to determine how much of the propylene oxide which is produced in the unspent salt medium is actually formed from some unspecified catalytic reaction using unspent salts and how much propylene oxide is produced from the co-oxidation of C_2H_6 by peroxide, which would be formed in situ in the unspent medium. Again, we have a situation, where it is difficult to determine whether higher olefins have been directly epoxidized by molecular O_2 , or whether another variant of co-catalysis by hydroperoxides or

2.3. Gas phase epoxidation using bifunctional, heterogeneous catalysts

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One of the most current and promising areas of high $\delta^{13}\text{C}$ spatiotemporal variation, which circumvents many of the uncertainties and difficulties mentioned above, involves the use of novel, bifunctional heterogeneous catalysts which apparently function by promotion of *in situ* H_2O_2 from H_2 and O_2 . The metallic components, which are supported on TiO_2 , which contains TiV sites which

activate the H_2O_2 for electrophilic addition to the C=C double bond of the substrate olefins. Hölderich and coworkers [20,21] have reported that propylene oxide can be produced using a bifunctional, heterogeneous catalyst composed of palladium supported on titanium siliclate (TS-1), or more preferably, platinum-promoted palladium supported on TS-1. The reaction, which is run as a liquid-phase slurry reaction typically uses a mixture of methanol and water as the slurry liquid. This bifunctional composition uses Pd, or Pt-promoted Pd to generate H_2O_2 from the H_2 and O_2 which are present, along with propylene, in the feed. Once formed, the H_2O_2 is activated by the appropriate Ti⁴⁺ sites on TS-1 support. Reaction of propylene with the activated hydroperoxide species, then forms propylene oxide. The obvious benefit of this catalyst system and feed composition is that expensive H_2O_2 is not required as the source of the hydroperoxide species, which is the catalyst for TS-1. Hölderich has examined the effects of different oxidants (H_2O_2 versus H_2 and O_2) and catalyst compositions (TS-1 and Pt/Pd/TS-1) for the production of propylene oxide. Key results, taken from [21] are shown, below in Table 2. The Pt/Pd/TS-1 catalyst was made using wet impregnation of an aqueous solution of $Pt(NH_3)_4(NO_3)_2$ and $Pd(NH_3)_4(NO_3)_2$ to give a composition of 0.1 wt.% Pt, 1.0 wt.% Pd supported on TS-1. The catalyst precursor was then thermally reduced (by the NH₃ ligands) by heating at 150 °C for 1 h in flowing N_2 . An autoclave charged with 0.2 g of 15.6 CH_3OH and 5.6 H_2O was sealed and 13 CH_3 (24 mol) and 7 bar H_2 (59 mmol), (10 bar O_2 (6 mmol), and 13 bar N_2 were used to pressure the reactor up to reaction conditions. When H_2O_2 was used as the oxidant, 8 g of 30% H_2O_2 were used in place of H_2 and O_2 .

The results show that the use of H_2O_2 as oxidant and TS-1 as catalyst is the best combination of oxidant and catalyst. The lower yield when H_2O_2 is used with the Pt/Pd/TS-1 catalyst is due to the decomposition of some of the H_2O_2 by the Pt/Pd part of the catalyst before it reacts with CH_3 . The use of H_2 + O_2 as the oxidant indicates that Pt/Pd is required for H_2O_2 formation. The lower yield for propylene oxide using H_2 + O_2 (5.3%) rather than H_2 + O_2 (21.3%) suggests that formation of H_2O_2 is rate limiting for propylene oxide formation. In addition to the limitations of Pt/Pd/TS-1 to form propylene oxide, the simultaneous addition of H_2 and CH_3 and H_2 and O_2 in the presence of noble metals such as Pt and Pd leads to severe yield losses by formation of CH_4 and H_2O , respectively. Hölderich has found that key to controlling reaction pathways to produce H_2O_2 and, subsequently, propylene oxide is that the Pt catalysts must be highly dispersed and preferentially exist as small, needle-shaped aggregates, rather than the more typical large, spherical-shaped particles. Calcination and reduction procedures for the impregnated $Pt(NH_3)_4(NO_3)_2$ and $Pd(NH_3)_4(NO_3)_2$ catalysts were critical in determining the final shape (size, versus spherical), size, and surface oxidation state (Pt^{4+} versus Pt^{2+}) of the final Pd catalysts. Not surprisingly, milder calcination (lower temperatures and lower O_2 concentrations) and reduction (lower temperatures and lower H_2 concentrations) conditions favored the formation of small, needle-shaped Pt aggregates that contained the largest fraction of surface Pt⁴⁺ sites. Because the concentration of surface sites correlated well with the formation rates of H_2O_2 , the surface concentration of Pt⁴⁺ was viewed as critical in determining maximum activity for the formation of propylene oxide. The addition of either amounts of Pt to Pt/TS-1 dramatically increased the concentration of Pt⁴⁺ relative to Pt²⁺. For 1 wt.% Pt/TS-1, the addition of 0.01 and 0.02 wt.% Pt increased the surface concentration of Pt⁴⁺ from 12% (no Pt) to 43 and 56%, respectively. Further increases in the amount of Pt up to 1.0% to give (1) weight ratio of Pt/Pd did not change the surface concentration of Pt⁴⁺. In addition, the shape of the Pt aggregates from primarily rod-shaped to a mixture of rod-shaped crystallites and the undetectable, spherical crystallites. Thus, the optimum level of Pt is a balance of increasing the

desirable surface concentration of Pt⁴⁺ with undesirable changes in the surface morphology of the Pt aggregates from needle-shaped to spherical. Further, since supported Pt catalysts are very active for the hydrogenation of C_2H_6 to C_2H_4 , excess loadings of Pt must be avoided.

Little attention has been directed to determining the site for H_2O_2 interaction with the H_2O_2 -activated surface. It is not clear whether there is direct interaction of gas phase C_2H_6 with the $Ti^{4+}-O-H$ site, or whether C_2H_6 is chelated on the Pt or Pd surface adjacent to the H_2O_2 -converted Ti⁴⁺ site. The latter possibility would suggest that propylene oxide formation occurs at the Pt (or Pt/Pd)-Ti⁴⁺ interface, such as at the edges of the needle-shaped, palladium aggregates in contact with the TS-1 structure. If this is the case, the combination of active, bifunctional sites will be quite limited, restricting the maximum rate of propylene oxide formation. The performance of this type of catalyst indicates the difficulty in forming a bifunctional catalyst having the correct composition, morphology, and distribution of active sites to give active and selective reactions of interest. Highly dispersed gold catalysts have been found to have exceptionally high activity for many types of oxidation reactions. In contrast, Hartati et al. [22] found that highly dispersed gold catalysts were active for CO oxidation at temperatures as low as -50 °C. These results, which were first reported by others [23], preceded the discovery that Cu^{2+} could be selectively oxidized to propylene oxide using $H_2 + O_2$ as the selective oxidant. For a much more complete list of various reactions catalyzed by supported gold catalysts, see the excellent review by Bond [23].

Hartati has found that that selective epoxidation of C_2H_6 occurs for gold particles supported on TiO_2 , when the Au particles exist as hemispherically-shaped particles, preferentially between 2.0 and 4.0 nm in diameter. For example, vapor phase epoxidation, using 0.50 g of 0.98 wt.% Au/TiO₂ at 50 °C in a gas mixture of C_2H_6 / O_2 / Ar = 10:10:10, at a total flow of 33.3 cm³/min gave 99% selectivity to propylene oxide; however, conversion of C_2H_6 was only 11%. Conversion of H_2 was 3.2%, indicating much of the H_2 was oxidized to H_2O , not H_2O_2 . Increasing the temperature to 80 °C resulted in preferential combustion of H_2 and C_2H_6 to H_2O and $H_2O_2CO_2$, respectively. Thus, selective operability is limited to an upper temperature of approximately 50 °C.

Table 2
Epoxidation of propylene.

Catalyst	PO_2 yield (%) (based on C_2H_6 conversion and PO formed)
TS-1	19.3
1 wt.% Pt/1 wt.% TS-1	21.3
TS-1	0
$H_2 + O_2$	5.3
0.1 wt.% Pt/0.1 wt.% TS-1	5.3

Catalysts containing gold particles <2 nm diameter primarily formed C_3H_6 . From the selective hydrogeneration of C_3H_6 , catalyst containing gold particles >4 nm in diameter were still selective for propylene oxide formation; however, the rate of formation, based on Au loading, decreased due to lower concentration of active Au sites as particle size increased. Formation of small, supported Au particles is accomplished by a deposition–precipitation technique, rather than the usual method of wet impregnation of a soluble gold salt, followed by calcination/reduction. Gold is deposited on the TiO_2 surface by precipitation of $\text{Au}(\text{OH})_3$ from a basic solution of chloroauric acid at $\text{pH} = 10$ onto the TiO_2 support. After washing to remove the residual Cl^- , the catalyst was calcined at 400°C to form the gold particles. Only by using the deposition–precipitation technique could hemispherical Au particles with diameters between 2.0 and 4.0 nm be prepared.

Chen and Ingallin's [22] work has proposed the following mechanistic scheme in Fig. 1 to explain the features of these gold catalysts for the epoxidation of C_3H_6 .

In this scheme, O_2 is inserted into a bridged $\text{Ti}^{4+}=\text{Au}^+$ site to form an activated molecular oxygen species.

Reaction with H_2 forms the hydroperoxy

species, which after elimination of H_2O , gives the bridging peroxy moiety. Presumably, this is the active oxygen species that reacts with C_3H_6 to form propylene oxide; although the bridging hydroperoxy species could also selectively react with C_3H_6 to form propene oxide. The site for C_3H_6 adsorption with increasing time on-line (catalyst deactivation) also

is not obvious in the above scheme, although it is believed that C_3H_6 is adsorbed and that adsorption of C_3H_6 on unsupported Au sites. Better work by Kensi [20] using ESR methods has shown that C_3H_6 is chemisorbed on non-oxygen covered Au surfaces through the interaction of the π -bond of C_3H_6 with an sp^2 bond of a gold surface atom. Interestingly, Kensi found that, either C_3H_6 or C_3H_6 chemisorbed on clean Ag surfaces, pre-adsorption of oxygen on Ag was necessary for olefin adsorption to occur. In agreement with many studies involving the adsorption of olefins on Ag surfaces, e.g. ethylene on $\text{Ag}(111)$ surfaces [31], 1-butene on $\text{Ag}(110)$ surfaces [32], and 1,3-butadiene on $\text{Ag}(110)$ surfaces [33].

The proposed role of the $\text{Ti}^{4+}=\text{Au}^+$ site in the above mechanism implies that propylene oxide formation occurs at the interfacial edge of the hemispherical Au particles and the TiO_2 support. This is consistent with the recent results of Nishizuka et al. [34], who compared the catalytic activities of gold dispersed on TiO_2 and $\text{TS}-1$ supports. The authors found that for similar gold weight loadings and crystallite sizes the activity of the supported TiO_2 catalyst was greater than that of the $\text{TS}-1$ catalyst. They concluded that the interfacial contact of the Au particles with TiO_2 resulted in the formation of more $\text{Ti}^{4+}=\text{Au}^+$ sites than when $\text{TS}-1$ was the support, since the Ti contained and surface concentration of Ti^{4+} sites is higher for TiO_2 than for $\text{TS}-1$. The authors also concluded that one of the primary causes for the generally observed low propylene oxide yields and discoloration of AuTiO_2 catalysts with increasing time on-line (catalyst deactivation) also

is the loss of the active site due to the loss of Au particles by calcination at high temperatures in air. Likewise, conversion of H_2 is high, with excess generation of H_2O . For the above reaction conditions, the smaller H_2 -Olefin epoxide oxide ratio varied between 13 and 18, indicating that most of the H_2 was oxidized to H_2O rather than H_2O_2 .

3. Epoxidation using molecular oxygen

With few exceptions, all direct epoxidation reactions using O_2 as the oxidant are heterogeneous, silver-based catalysts that are promoted to greater or lesser extent with alkali and/or alkaline earth promoters. Chlorine is also used as a reaction moderator, and it is added either during preparation, or added during reaction conditions by decomposition of organic chloride in the feedstream. Because of the importance and current volume of anhydride oxide, almost all effort has focused on selective epoxidation of propylene. The recent demonstration that chlorite, longer than propylene, such as 1,3-butadiene, styrene, and norbornene, can also be epoxidized has shifted some attention toward these potentially important reactions and chemical intermediates. The following discussion will first discuss the development and use of the Au for propylene epoxidation, before the discussion of higher olefin epoxidation.

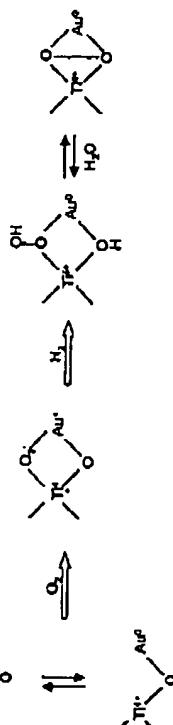


Fig. 1. Probable mechanism for the formation of the active oxygen species on AuTiO_2 catalyst.

observed in Clerici and Ingallin's [22] work is the strong adsorption of propylene oxide on the catalyst. The dependence of strongly-bound olefin epoxide products and the subsequent effects on catalyst design will be discussed in more detail when the epoxidation of higher olefins, such as 1,3-butadiene, over supported silver catalysts is discussed.

It is possible to calculate the upper limit of catalytically-active sites for supported AuTiO_2 catalysts. The 0.98 wt% AuTiO_2 catalyst evaluated and characterized by Clerici and Ingallin [22] contained Au particles with a mean diameter (measured by transmission electron microscopy) of 2.4 nm. Using the solid state parameters from Anderson [35], we can calculate the dispersion of 2.4 nm Au particles on the perimeter of the hemispherical Au particles are active (since the active site is postulated to be a bridged $\text{Ti}^{4+}=\text{Au}^+$ species), then the effective dispersion of the Au particles decreases to 0.11. This gives an upper limit of the concentration of active sites, since not all the Au sites on the interfacial perimeter of Au and TiO_2 will be coordinated to Ti^{4+} sites. The propylene oxide formation rate reported by Hwang was 0.20 cmol/(g Au), corresponding to 3.24×10^{16} PO_3 molecules/(g Au). The above catalyst contained a maximum of 3.2×10^8 Au sites/cm², resulting in a turn over frequency for propylene oxide formation = 0.01 s^{-1} . Turnover frequencies in this range are approximately 20–100 times lower than reported turnover frequencies reported for alkylene oxide and epoxidation of C_3H_6 . This catalyst is dramatically improved for propylene oxide and space time yields of propylene oxide must be dramatically improved for this system to become commercially-viable. Other problems include catalyst deactivation, which may be partially due to yet another problem with supported Au catalysts, that of preventing particle sintering under reaction conditions.

Regardless, the potential of this route has attracted the attention of a number of chemical companies and patents have recently applied claiming selective production of propylene oxide using gold supported on various Ti-containing supports [36–42]. Most of these patents are concerned with proprietary advances that claim higher space time yields of propylene oxide and longer catalyst lifetimes under reaction conditions.住友化学技術センター - (株)

Although promoted silver catalysts normally used for ethylene epoxidation are synthetically non-selective for propylene oxide formation, due to the high reactivity of the allylic C–H bonds [43], a number of research efforts have shown that heavily-modified silver catalysts do show improved selectivity to propylene oxide. Compared to silver catalyst compositions used for ethylene oxide formation, these catalysts have much higher silver, alkali metal, alkaline earth, and chlorine loadings and, thus, are quite different in terms of

Under physical and chemical properties. In some compositions, the modified silver compositions is even unsupported. During preparation, the components of the catalyst are mixed into a liquid slurry, rather than being deposited using wet impregnation or incipient wetness methods onto a support, and then ball-milled to ensure even mixing and distribution of components before drying and calcination. The earliest work was reported by Kolombos and McCall [44] for a series of catalysts that were prepared by mixing a silver powder with various group IIA metal halides, specifically MgCl_2 , CaCl_2 , and BaCl_2 , which after drying, gave compositions containing between 91 and 95 wt-% silver, with the balance being a group IIA metal chloride. Evaluation of these catalysts at 240–290 °C in a gas stream of 3% C_3H_8 , 70–80% O_2 , balance He gave selectivities to propylene oxide of 12–16% at propylene conversions between 80 and 90%. While these results were clearly marginal, they were much better than propylene oxide selectivities for silver catalyst compositions used for ethylene oxide production.

Later work by Thornton [45] extended the study of heavily-modified, silver catalysts. A catalyst composed of 40 wt-% Ag and 1.5 wt-% K supported on or mixed with CaCO_3 (which itself can be considered to be a promoter as well as a support) was exposed to a feedstock of 10% C_3H_8 , 9% O_2 , 200 ppm $\text{C}_2\text{H}_5\text{Cl}$, and balance N_2 at 245 °C. Propylene conversion was 24% at selectivity to propylene oxide of 47%.

Litwak, Bowman [46] prepared and evaluated a series of catalysts, characterized by having high loadings of Ag (approximately 60 wt-% Ag) and produced with high, but unspecified, loadings of group IIA salts and supported on sodium silicate. Among the different catalysts, performance of a Mg-promoted catalyst at 180 °C in a flow stream of 65% C_3H_8 , 25% O_2 and 2% H_2O water at a 100% high purity (99.999% C_3H_8) gave a selectivity to propylene oxide of 47% at 3.7% C_3H_8 conversion. However, the low GHSV needed to attain 3.7% conversion underscores the low activity of this catalyst system.

The intrinsically low activity of these types of catalyst systems has been addressed by Lu and Zuo [47] for an unsupported Ag catalyst promoted with NaCl or BaCl_2 . Reaction temperatures as high as 390 °C at a GHSV of 24,000 h^{-1} (or a gas stream of 5% C_3H_8 , balance air resulted in conversion of 49% of C_3H_8 at 25% selectivity to propylene oxide. Even at these short

contact times, the selectivity is unusually high. The authors claim that NaCl and BaCl_2 are better promoters than comparable loadings of NaCl and LiCl , indicating that the catalyst performance is partially due to the Na^+ and Ba^{2+} cations, not just the Cl^- anion. Promoter loadings either lower or higher than 3.8–4.5% NaCl gave catalysts with lower activity and selectivity.

Most of the reported work for oxidation of propylene by heavily-modified, high weight loading of Ag catalysts have been carried out by Gaffney and co-workers [48–53]. Catalyst compositions investigated by Gaffney include the following components and ranges of composition: 30–60% Ag, 0.5–3% K, 0.5–1% Cl, 0.5–2.5% Mo, 0.5–1% Re_2O_7 , 0.5–1% W_2O_8 , and balance CaCO_3 . At these weight loadings of Ag and other promoters, it is not realistic to consider CaCO_3 as a support, since in some cases, it is a minority component. Sharts of the components which powdered CaCO_3 are ball-milled, thoroughly mixing the CaCO_3 with the other components. After drying and calcining, the powder is pressed and shaped into tablets or other preferred shapes. Gas phase feed compositions were typically 10% C_3H_8 , 5% O_2 , operating 5–25% CO_2 , and balance N_2 or other inert ballast gas, as well as 50–500 ppm organic inhibitor (typically ethyl chloride), and 20–300 ppm NO . Most of the reactions were conducted at 250 °C at 10 (bars) pressure at a total GHSV of 1200 h^{-1} .

Gaffney showed that the complex recipe of catalyst components and gas phase promoters was required for both activity and selectivity to propylene oxide. Thus, a catalyst composed of 30 wt-% Ag and 50 wt-% CaCO_3 gave only 3% selectivity to propylene oxide, while a catalyst with 1% Ag, 1% K_2O and CaCO_3 without any organic chloride or NO feed producer gave low conversion (<1%) and low selectivity (<3%). Co-feeding O_2 and NO_2 along with C_3H_8 and O_2 enhanced both conversion (up to 10%) and selectivity (up to 60%). The role of NO_2 is poorly understood, although one hypothesis is that adding NO_2 maintains a critical concentration of NO_3^- on the catalyst surface, although there is no explanation as to why NO_3^- is needed to enhance performance. The role of NO_2 is further complicated by the observation that a catalyst containing Mo as a promoter has the same activity and selectivity with or without NO_2 in the feed. The levels of ethyl chloride used with this process (typically about 200 ppm) are many times higher than the levels

currently used in either the specification of ethylene or butadiene. In the latter cases, typical levels of organic chlorides in the feed vary between 1 and 5 ppm [34,55]; levels higher than 5–10 ppm would result in continuous loss of activity for ethylene oxide and epoxybutane formation.

Even though the performance of this catalyst system is better than for the other propylene epoxidation operations discussed above, the propylene oxide yield is still too low for commercial use. For a reactor to activity of 3.296 conversion at 50% selectivity to propylene oxide using 2 cm^3 of catalyst at 30 psig and 245 °C, the calculated space time yield is 0.7 h (propylene oxide)/(1 m³ h), which is at least an order of magnitude lower than ethylene oxide and epoxybutane production rates.

It is very difficult to determine any kind of catalyst surface structure–catalyst performance correlation from these catalysts, since surface compositions of these complex catalysts are so poorly defined. Not only are the concentrations of Ag, K, Cl much higher than commonly used to prepare ethylene oxide catalysts, the catalyst components are not distributed onto the CaCO_3 by wet impregnation or incipient wetness, but are actually thoroughly mixed with the CaCO_3 during preparation. Thus, it is not possible to determine whether the CaCO_3 functions primarily as a physical support, as a necessary component of the catalyst, or as a diluent for bulk silver.

If we consider these systems as a uniform mixture of silver and CaCO_3 , the catalytic properties should be addressed in terms of the well-known ligand and ensemble effects of catalysts [56], whereby catalytic behavior is influenced by either the electrostatic properties of Ag sites interfaced with CaCO_3 (Ligand effect), or by the values of coordination among Ag atoms that have different reactivity due to different sizes requirements (ensemble effect) that competing reactions. Ensemble effects are normally associated with metallic alloys, where the alloy surface can be atomically diluted into ensembles of contiguous atoms of the catalytically-active component. It is not obvious that the type of atomic dilution inherent in ensemble theory is going to occur from physical mixing of a Ag salt and CaCO_3 . Surface energies of Ag and CaCO_3 resulting from mixing should be much larger than 5–20 Å² atom aggregates typically considered to be relevant in catalysts. In fact, a correlation of Ag ensemble size

for propylene oxidation over Ag–Au alloys has been carried out by Gencen et al. [57], who found that for Ag–Au alloy surfaces that were rich in gold (>70% Au at surface), C_3H_8 was selectively oxidized to acetolene (propene oxide), propylene oxide was produced only at trace amounts and did not change with the degree of gold alloying. The authors argued that while formation of propylene oxide did not exhibit an ensemble effect, the selective formation of acetolene indicated that small ensembles of Ag atoms were sufficiently large enough to effect the allylic oxidation of propylene to acetolene, but were too small to allow consecutive oxidation of acetolene to CO_2 and H_2O . Combustion required a larger number of Ag atoms to permit overlap of adsorbed acetolene with adjacent O-covered Ag atoms.

The more logical possibility for the selective activity of the catalyst prepared by Gaffney is the existence of selective sites at the interface of the Ag and CaCO_3 portions of the catalyst. This need to support essentially their promote catalysts that are stampared essentially with high, levels of equal weights of Ag and CaCO_3 with high, levels of K and Cl to obtain in selective behavior may be effectively poison the conventional Ag sites existing on the surface of the exposed silver surface, leaving only the interface Ag– CaCO_3 sites. If this is the case, one major goal of catalyst development and potential area for future research should be directed to increasing the concentration of active and selective sites, since current catalysts have activities too low for commercial utility. Regardless, this family of catalysts should be considered as one of the more promising new systems for selective epoxidation of propylene to propylene oxide. Since almost all information regarding the structures and performance of this novel system exists in patents, this is one area that could greatly benefit from a detailed study of better characterized catalysts to help elucidate the nature of the active and selective sites for propylene oxide formation.

3.2. Epoxidation of 1,3-butadiene

Monnier and coworkers [3,53,58–60] have demonstrated that it is possible to selectively epoxidize higher olefins to their corresponding epoxides using supported silver catalysts as long as the olefins do not contain reactive, allylic hydrogen atoms. Using an unsupported Ag– Al_2O_3 catalyst, Monnier attempted

cases of propylene and 1-butene, respectively, only CO_2 and R_2O were formed. However, the results for butadiene indicated it was possible to epoxidize this non-satellite olefin to 3,4-epoxy-1-butene, the mono- α -epoxide of butadiene. However, after only 2–3 h on line, catalytic activity declined from 2.8 to 0.8% conversion. Selectivity to epoxypentene also declined from 75 to 45% non-selective products (undetectable to three products) changed from essentially CO_2 (25%) to a mixture of CO_2 (4%), formaldehyde (11%), acetone (25%), 2-butanol (15%), and a trace of 2,5-dihydrofuran (<1%) with the added reaction time. The disappearance of methanol, acetone, and formaldehyde, which are thermodynamically favored by 10–14 kJ/mol, hydrogenolysis of the C_5 – C_6 bond of an unspecificated C_4 -oxygenated intermediate provides a pathway for the formation of acetone and formaldehyde, both of which were formed in approximately 1:1 molar ratios during the epoxidation reaction. Finally, the pathway for 1,4-addition of oxygen across the ends of butadiene initially forms 2,5-dihydrofuran, which undergoes facile allylic oxidation to give furan. The 1,4-addition route is the one favored by Roberts et al. [33] who analyzed by mass spectrometry the thermal desorption products in Fig. 2 were sequentially added to the reactor feedstocks during the epoxidation reaction. The results, which are shown in Table 4, indicate that (a) furan does not undergo further reaction, (b) 2,5-dihydrofuran is selectively oxidized to furan, (c) crotonaldehyde, or 2-butenal, is only slightly oxidized to $\text{CO}_2/\text{H}_2\text{O}$, and (d) epoxypentene is not only converted to furan (via 2,5-dihydrofuran), isopentenol, crotonaldehyde, and CO_2 , only 55% of the epoxypentene which was added could be accounted for. Thus, epoxypentene was the only reaction intermediate that could account for all observed reaction products (and in the appropriate ratio) during butadiene epoxidation. Furthermore, the net rate of epoxypentene formation was greatly suppressed during the period of time that epoxypentene was externally added to the reactor feedstream. The activity was slowly restored when epoxypentene was removed from the feed, indicating a strong kinetic inhibition by epoxypentene for the formation of epoxypentene. This strongly-bound epoxypentene was also the reason for poor accountability of epoxypentene when it was added to the feedstream.

The results from co-feeding of epoxypentene suggested that all reaction products could be satisfactorily explained by the direct 1,2-addition of oxygen to adsorbed butadiene to initially form epoxypentene.

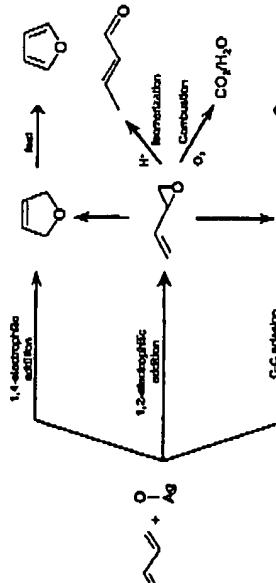
The strong adsorption of epoxypentene resulted in rearrangement to form 2,5-dihydrofuran and furan as well the hydrodepolymerization products, acetone, and formaldehyde; the strong adsorption also explained the kinetic inhibition effect of epoxypentene. Although the preference for 1,2-addition of oxygen to one of the localized C–C double bonds of butadiene is not predicted by the thermal desorption work of Madix,

Table 1
Oxidation of olefins over supported 5% Ag/2% Cr_2O_3

Reaction	Selectivity (%)	Conversion (%)
$\text{CH}_2=\text{CH}_2 + \text{O}_2$	51	12
$\text{CH}_2=\text{CH}_2 + \text{O}_2$	47	7
$\text{CH}_2=\text{CHCH}_3 + \text{O}_2$	0	92
$\text{CH}_2=\text{CHCH}_3$	4	8
$\text{CH}_2=\text{CHCH}_2 + \text{O}_2$	91	92
$\text{CH}_2=\text{CHCH}_2$	9	1.2
$\text{CH}_2=\text{CHCH}_2 + \text{O}_2$	92	1.2
$\text{CH}_2=\text{CH}_2$	0	2
$\text{CH}_2=\text{CHCH}_2 + \text{O}_2$	2	1.8
$\text{CH}_2=\text{CHCH}_2$	22	1.2
Furan	12	72

* Reaction temperature = 250°C and feedstream = butadiene/ O_2 = 31:1.

the epoxidation of a series of olefins. The results, summarized in Table 3, indicated that while the observed selectivity to epoxide oxide was expected for an unpromoted catalyst, the selectivities to propene oxide and butylene oxide were non-existent. In addition to small amounts of the selective allylic oxidation products (acetone and butadiene in the

Fig. 2. Chemical mechanism scheme for Cr_2O_3 epoxidation.

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epoxidation, the thermal desorption products of butadiene oxidized on an oxygen-poor-supported $\text{Ag}/1.0$ surface and contributed the desorption products were primarily 2,5-dihydrofuran and furan. In later thermal desorption studies of 1-butene from $\text{Ag}/1.0$ surfaces, Roberts et al. [32] concluded that 1-butene was oxidatively dehydrogenated to form 1,3-butadiene, which then underwent 1,4-addition to initially form 2,5-dihydrofuran. In agreement with the above results, Schlett and Jorgenson [66] used extended Hückel calculations to determine the geometry of the intermediate of butadiene on oxygen-poor-supported $\text{Ag}/1.0$ planar surfaces and calculated that 1,4-addition of oxygen to form 2,5-dihydrofuran is thermodynamically favored over 1,2-addition to form epoxidant. The mechanism of Madix and calculations of Jorgenson did not provide any reasonable pathway for the formation of epoxypentene. Previous results for oxidation of butadiene using supported silver catalysts corroborate the results of Madix and Jorgenson. Furthermore and Hwang [67] and Rao [68] evaluated 10% Ag/BPO_4 and 70% Ag/MnO_2 , respectively, as catalysts for butadiene oxidation and found that, in both cases, the preferred oxidation product was furan which was formed by oxidation of 2,5-dihydrofuran as the primary product. Neither catalyst, however, was very active or selective for furan formation.

The difficulty with the above results is that the formation of epoxypentene is not satisfactorily explained. Thermodynamically, the isomerization of 2,5-dihydrofuran to form epoxypentene is unfavorable by 19.5 kcal/mol. To determine which, if any, of the reaction pathways in Fig. 2 was dominant during butadiene epoxidation, realistic concentrations of each

Addition of reaction products to butadiene during butadiene epoxidation				
Product	Crotonaldehyde	2,5-DHF	Epoxypentene	
Furan	N/A	0	0	73
Acetone	0	0	0	0
2,5-DHF	0	N/A	0	0
Epoxypentene	0	0	N/A	55
Crotonaldehyde	0	0	N/A	25
CO_2	0	0	6	24
CO	0	4	16	14
Conversion of additive (%)	0	4	100	100
Accountability of additive (%)	100	100	97	97

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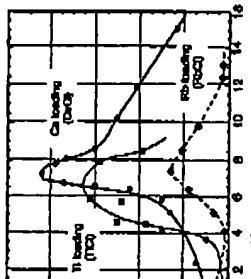


Fig. 1. Fluorocarbon loading vs. catalyst performance. Reaction temperature = 210°C, feed composition is $\text{m-C}_6\text{H}_4$: $\text{m-C}_6\text{H}_4\text{Cl}$: $\text{m-CH}_2\text{Cl}$ = 4:1:1 or $\text{GHSV} = 5000\text{ h}^{-1}$. Substituents to oxygenate are present in optimum loading: C_6Cl_4 = 94.3%; BzCl = 93.9% and

selectivity of 82–84%, which is much lower than the 96% reported by Monnier et al. The long-term stability of epoxypentane in water in the presence of epoxidase at 30 °C and 100% extraction temperatures are also questionable since it is known that epoxypentane is hydrolyzed by water [3–4].

The curves in Fig. 3 show that prononciamto by CrCl_3 reaches a maximum activity of approximately 950 ppm at 100 °C, or 70 $\mu\text{mol} \text{ Cr}_2\text{O}_7$. For this family of supported catalysts, likewise, prononciamto by RhCl_3 and TiCl_4 also indicates that loadings of approximately 100–150 $\mu\text{mol} \text{ Rh}$ and Ti_2Zr_2 result in maximum activity for epoxypentane isomerization. Catalytic prononciamto by CrCl_3 over the same concentration range did not exhibit any significant enhancements in either activity or selectivity. Performance was essentially the same as for unsupported catalysts. Reaction conditions for the promoted catalysts were 2.5% $\text{Ag}/\text{Al}_2\text{O}_3$ catalyst at all cases were a bar pressure and 210 °C using a feed composition of $\text{C}_2\text{H}_5\text{CH}_2\text{CH}_2\text{O}_2 = 4:1:1$ in $\text{C}_2\text{H}_5\text{CH}_2 = 540 \text{ g} \text{ mol}^{-1}$. It is interesting that optimum promoter loadings of Cr_2O_7 and Ti_2Zr_2 occur at similar molar loading levels, suggesting a specific and common type of interaction between the promoter and the silver surface. Then the interaction

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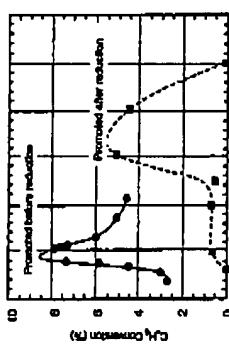


Fig. 4. Effect of Al and reduction on promoting the polymerization of α -methylstyrene. Reaction temperature = 210°C, feed composition 1,000-
 $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5/100\text{Al}_2\text{O}_3$, $\text{C}_6\text{H}_6 = 41.1$ ml./G. $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5 = 100.0$ ml./G.

and at the promoter salt occurs with the silver surface, and the α -Al₂O₃ support, can be inferred from the curves in Fig. 4 for two series of catalysts which have been promoted at different stages of preparation. The sample promoted before reduction of the Ag salt, the precursor shows a sharp maximum at approximately 950 ppm Cs, while the sample promoted by Cs after reduction of the silver salt to Ag_0 -Al₂O₃ yields a broad maximum between 200 and 350 ppm Cs. The reduction of the optimum promoter loading at higher Cs loading suggests that Cs is deposited on both the Ag and Ag_0 surfaces of the catalyst, while in the case of co-interaction of the Ag and Cs salt, Cs is targeted much more effectively onto the Ag surface. Likewise, the interaction of the Cs promoter appears to be more effective when deposited before reduction of the Ag salt, since bimetallic conversions are substantially higher (93% compared with 5.5% conversion, respectively), when the promoter is added before reduction.

Table 5	Properties of parameterizations for background spotter data			
Column (4)	Isotropic radius (km)	Chandrasekhar radius (km)	Periodicity	Periodicity
Lithium	0.78	0.120	0.01	0.01
Scandium	0.97	0.081	0.01	0.01
Potassium	1.13	0.045	1.14	1.14
Rubidium	1.40	0.025	1.54	1.54
Caesium	1.65	0.020	2.54	2.54
Thallium	1.40	0.010	4.14	4.14
Lead	1.26	—	—	—

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cessful promoters are large and highly polarizable ions under reaction conditions. As stated above, catalysts with a high K^+ salt are not active for epoxynate formation, suggesting that this salt is not the critical factor in determining promoter efficiency. If promoter anions function merely by blocking, or neutralizing, anion-selective sites, then K should show some promoter selectivity for epoxynate formation, based on size and reactivity of alkali metals. Polarizability or the ionic radius of an ion's ability to deform its electronic core to accommodate external electric fields, may be a more important factor in determining promoter efficiency than size alone.

Polymer optimized for epoxynate production, at 900–1000 ppm level of Ca F_2 loading is substantially higher than the 200–300 ppm Ca loadings typically used for ethylene oxide formation [75]. In addition, a catalyst optimized for epoxynate formation is essentially inactive for ethylene oxide, while a catalyst optimized for ethylene oxide formation is relatively active for epoxynate [3]. These results clearly indicate the impact of differences in kinetics on promoter requirements for otherwise similar reactions. For epoxynate formation, the rate limiting step involves desorption of epoxynate [3], while for ethylene oxide formation, the rate determining step is considered to be the surface reaction between adsorbed ethylene and adsorbed oxygen [34]. However, in both reactions, the active oxygen used to form the epoxynate is atomic oxygen [76,77], and not molecular oxygen [54]. Application of the 6.77% salt that has been used to rationalize the role of molecular oxygen in ethylene epoxidation to the selectivity of epoxynate to O_2 (11.2, or $>91\%$). Selectivity values in Marmur and coworkers [54,78–81] have been reported

weight loadings of Na, K, Li, and Cs between 7000 and 60,000 ppm/g- Ag were used to promote the supported silver catalysts for the epoxidation of styrene, such as styrene [73] and 1,3-dimethyl-1-butene [58] and hundred allylic alcohols, such as nonbenzenes [74], using Cs- and Rb-promoted silver catalysts; results are summarized in Table 6. The data for the epoxidation of styrene and 4-methylpyridine show that these catalysts are both active and selective for the formation of their respective epoxides, and corroborate earlier work by Blum [80]. For unsupported silver catalysts and by Harker et al. [76] for temperature-programmed reaction spectroscopy of styrene adsorbed on oxygen-covered $\text{Ag}(111)$ single crystal surfaces. However, in the examples of Blum,

reported on $\alpha\text{-Al}_2\text{O}_3$ that was exposed to a stream of 10% O_2 at 2% to 4% conversion, and 85% at 3600 h⁻¹ space velocity and 230 °C, gave 66% conversion of styrene at a selectivity to styrene oxide of 95%. It is not obvious why the catalysts evaluated by Blum contained much higher levels of promoter salts; no data were included for catalysts with lower promoter loadings. The results in Table 6 indicate that the presence of the *para*-C-H group in 4-methylstyrene results in combustion of this olefin to $\text{CO}_2/\text{H}_2\text{O}$. While the C-H group is not allylic to the vinyl group, it is both allylic and benzylic to the aromatic ring, and is very reactive towards C-H bond breaking during oxidation. This reactivity and subsequent combustion of 4-methylstyrene prevents formation of the epoxide. Teri-styryl ethoxides, another allylic olefin in Table 6, is also very selectively epoxidized; however, the bulky tert-butyl group lowers reactivity of this olefin.

The results for epoxidation of nonbenzenes in Table 6

indicates that Cs-promoted silver catalysts also selectively epoxidize allylic olefins to their corresponding epoxides, as long as the allylic C-H groups are kinetically nonreactive. The results for nonbenzenes agree well with the temperature-programmed reaction spectroscopy results of Roberts and Madriz [77], who observed that nonbenzene epoxide is formed at approximately 310 K from $\text{Ag}(110)$ surface which had been pre-adsorbed with aromatic and aromatic oxygens. In a related study, Cai et al. [81] reported that during continuous oxidation of nonbenzene by molecular oxygen over an unsupported silver-supported catalyst only benzene was formed as the oxidation product. The authors concluded that nonbenzene oxide was not an intermediate during formation of benzene. Data from Monnier and Muehlemer [79] for unsupported silver catalysts confirm that only trace amounts of nonbenzene oxide are produced by unsupported catalysts, but that Cs-promoted silver catalysts are very active and selective for epoxide formation. The results of Cai et al. are consistent with nonbenzene epoxide being the primary product, but that the strongly-bound nonbenzene epoxide undergoes hydrogenolysis and oxidative dehydrogenation to form benzene, in a manner analogous to acrolein and furan formation during epoxidation of furadene over unsupported silver catalysts.

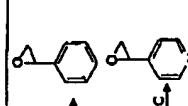
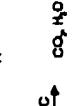
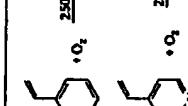
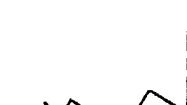
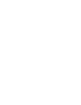
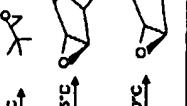
The importance of ensuring that olefins contain no reactive, allylic C-H bonds is seen by comparing the

selectivity differences between epoxidation of nonbenzene and bis(2,2,2)-bicyclo[2.2.1]hept-2-ene. Epoxidation of bis(2,2,2)-bicyclo[2.2.1]hept-2-ene is only 3.0% selective to the desired epoxide. The addition of the additional $-\text{CH}_2$ group in the bridging position results in a dramatic decrease in selectivity, presumably because the less pinched geometry of bis(2,2,2)-bicyclo[2.2.1]hept-2-ene makes the allylic hydrogen more accessible and reactive with the Ag-O surface. It is not possible to state whether the more favorable C-H bond angle of the allylic C-H bond, or the lower strain energy of the stylic structure (after C-H bond rupture), are responsible for the lower observed selectivity to the olefin epoxide. However, comparison of these two bicyclic olefins towards olefin epoxidation does underscore the importance of having no reactive, allylic C-H bonds for selective epoxidation to occur using supported silver catalysts.

4. Conclusions

Recent developments in olefin epoxidation have indicated it is possible to epoxidize higher olefins directly by using molecular oxygen, or indirectly by using molecular oxygen to generate an active and selective oxidant *in situ* during reaction. The community-practiced methodology of systematic and minor modifications of pre-existing catalysts and technology. In this case, the coordination of ethylate, have not been successful in advancing olefin epoxidations. In each instance of successful epoxidation of higher olefins, di-*conformational* changes from traditional approaches have been required. One novel approach has recognized that while it is known that H_2O_2 is active and selective for epoxidation, the high cost of H_2O_2 has prevented its use as a practical oxidant. However, the *in situ* generation of H_2O_2 from H_2 and O_2 under alichemical epoxidation reaction condition is a potentially inexpensive way to combine H_2O_2 with conventional olefin epoxidation catalysts, such as TiS_1 and TiO_2 . These bifunctional catalysts have combined new catalytic components that generate H_2O_2 *in situ* with the functional component that activates H_2O_2 for olefin epoxidation. Generation of H_2O_2 from H_2 and O_2 is a difficult research problem, especially in the presence of an olefin. Not only one must be concerned with selective use of H_2 and O_2 to generate H_2O_2 , and not H_2O , the competing hydrogenation reaction of the

Table 6
Epoxidation of other olefins using $\text{Cs}(\text{C}_{2}\text{H}_5\text{O})_3/\text{Ag}(\text{Al}_2\text{O}_3)$ catalysts

Reaction	Molar selectivity (%)	Conversion (%)
 + O_2 $\xrightarrow{250^\circ\text{C}}$ 	93	19
 + O_2 $\xrightarrow{245^\circ\text{C}}$ 	93	21
 + O_2 $\xrightarrow{225^\circ\text{C}}$ $\text{CO}_2/\text{H}_2\text{O}$	0	100
 + O_2 $\xrightarrow{250^\circ\text{C}}$ 	95	1.5
 + O_2 $\xrightarrow{225^\circ\text{C}}$ 	92	43
 + O_2 $\xrightarrow{210^\circ\text{C}}$ 	36	4

olefin to form the corresponding paraffin is another bimolecular reaction that must be suppressed. Current bimolecular catalysts use either a combination of noble metal components, such as Pt-Pd, to generate H_2O_2 , or the unique properties of small supported gold particles to generate H_2O_2 . In both cases, the primary limitation of these bifunctional catalysts are the low rates of H_2O_2 formation (and subsequent low rates of olefin epoxidation) and the non-selective consumption of H_2 (which generates H_2O_2) and olefins (which generate paraffins). Olefin problems include the stability of these bifunctional compositions under reaction conditions and the potential flammability hazards associated with handling gas mixtures containing both H_2 and O_2 .

Another novel approach employs silver-based methodology, but in much different combinations of weight loadings of silver, promoters, and supports than typically used for propylene epoxidation. These catalysts, which have been used for propylene epoxidation, have much higher silver, alkali metal, alkaline earth, and catalytic loadings than the analogs used for olefins oxide formation, and are quite different in terms of their physical and chemical properties. The silver and promoters are not supported to these compositions, but are actually uniformly mixed with the carrier, typically alkali earth carbonates, such as CaCO_3 . In some compositions, the unmodified silver composition is even unsupported. While the selectivities to propylene oxide are considerably higher than conventional silver catalysts, selectivities and rates of olefin epoxide are still too low for commercial application. However, the improved performance of these catalysts is noteworthy. Since almost all information regarding the structure and performance of this novel system exists in patents, this is one area that could greatly benefit from a detailed study of better characterized catalysts to help elucidate the nature of the active and selective sites for propene oxide formation.

Yet another approach has been to use silver-based catalysts for the selective epoxidation of non-olefinic olefins, recognizing that the reactivity of allylic hydrogens makes the use of conventional silver-based catalysts unrealistic. Although the kinetic slow step for epoxidation of higher, non-olefinic olefins is different from that for olefins epoxidation, changes in the promoter loading levels have permitted the selective

epoxidation of olefins such as 1,3-butadiene, styrene, and kinetically-stabilized olefins, such as isobutene. This has led to the commercialization of butadiene epoxidation to form epoxidized-the first olefin epoxide to be commercially-produced since ethylene oxide was commercialized.

In summary, direct olefin epoxidation by molecular oxygen is an extremely important class of catalytic reaction. The recent examples of progress discussed in this article indicate that there is much left to exploit in direct epoxidation of higher olefins. Many of the compositional and structural features of these novel catalysts are poorly understood. Likewise, many of the kinetic features and reaction intermediates of higher olefin epoxidation remain to be elucidated. There are areas of catalytic research that, if successful, would have tremendous implications on growth of the chemical process industry as a time when many believe that the chemical industry is at a time when many believe that a class of chemical compound are arguably one of the most versatile families of chemicals produced today.

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